Selective Removal of Nitrogenous Compounds Using Zeolites

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Introduction
     Various sorbents have been used in the past for the selective removal of nitrogenous compounds. Supported ferric chloride (1), macroreticular ion exchange resins (2-4), basic and neutral alumina (5), and acid modified silica (6) can selectively remove nitrogenous compounds from petroleum fractions. These separation methods however were designed for small scale analytical separation. Recently there has been some interest in large scale separation of nitrogenous material (7-9). This interest stems from the possibility of using an adsorption (or sorption) process as a substitute for the expensive hydrotreating process.
     This paper describes the selective removal of nitrogenous compounds from naphthas using zeolites. The selectivity was determined for several zeolites using a model compound solution. The selectivity strongly depends on the nature of the compound. The zeolite was cation exchanged in order to modify the selectivity.

Experimental
     The model compound solution was prepared by dissolving the appropriate amount of compound in reagent grade toluene. The composition of the two solutions are given in Table 1.
     The zeolites obtained from BDH Chemicals were shaken over night in a 1M aqueous solution. The chloride salt of the cation to exchange was used. The zeolite was then filtered, washed, and dried at 110°C for 12 h. The zeolite was activated at 520°C in the presence of air for 12 h.
     A typical experiment involved pumping the feed continuously at 0.5 mL/min into a 30 cm long and 0.4 cm I.D. stainless steel column packed with the sorbent. Samples of the effluent were collected every 5 mL and subsequently analyzed using a Varian 6000 gas chromatograph equipped with a 30 m long DB-5 capillary column. For whole naphthas the effluent samples were analysed for total nitrogen by chemiluminescence using a Dohrman total nitrogen analyzer. All experiments were performed at room temperature. Three grams of zeolite was used for each run. Table 2 give the properties of the naphthas used in this study.

Results and discussion
     The sorption results for model solution 1 by zeolite 13 X in the sodium form are shown in Fig. 1. These results clearly show that the degree of sorption depends on the nature of the compound. Compounds such as benzacridine and tetrahydrocarbazole appear in the effluent after 20 mL whereas compounds such as benzylamine are still completely removed after 150 mL. There is an inverse correlation between the amount sorbed and the molecular size of a compound; the amount of three- and four-ring compounds sorbed is generally lower than that of two- and one-ring compounds. The relation between separation and molecular size is well documented (10-11); zeolites are known as shape selective sorbents because of their uniform pore size. Smaller pore size zeolites were tested using solution 1. The efficiency of separation was proportional to pore size.

The previous results indicate the difficulty of removing all nitrogenous compounds indiscriminately. The separation is diffusion-controlled and larger molecules are not removed to any great extent. The model compound study suggests that zeolites would be most effective for the treatment of naphthas which contain small nitrogenous compounds. An experiment was therefore carried out using zeolite 13X and two naphthas (Fig. 2). Using the area over the breakthrough curve the sorption capacities were calculated. The capacities were: 4.61 mg N (1.36 mg N/g zeolite) for the coker naphtha, and 14.24 mg N (4.3 mg N/g zeolite) for the hydroprocessed naphtha which is significantly lower than the 298 mg (100 mg N/g zeolite) obtained for the model compound solution 1 and the 332 mg obtained for model compound solution 2. Solution 2 is more representative of a naphtha since it contains smaller nitrogenous compounds than solution 1. Both solutions give a capacity of 10% by weight of zeolite.

The sorption capacity for the model compounds is similar to that obtained for vapour phase sorption of hydrocarbons and nitrogenous bases. Breck and Flanagen obtained a capacity of 0.227 g of tributylamine per gram of zeolite X at room temperature (12). In a liquid phase experiment $C_8F_{18}O$ was separated from $(C_4F_9)_3$ N by sorption on a zeolite 13X; the $C_8F_{18}O$ loading at breakthrough was 0.3 g/g of zeolite (13). The capacity obtained in this study demonstrates the possibility of using zeolites for large scale separation. The lower capacity obtained for naphthas suggests the competitive sorption of non-nitrogenous compounds; the sorbent may not be totally selective for nitrogenous compounds and substantial quantities of olefins or aromatics may be sorbed. No direct evidence for this is presented in this study. These aspects are presently under study. The aim is to improve the selectivity for nitrogenous compounds, specifically for multi-ring compounds.

The selectivity shown by a sorbent toward a sorbate is determined by several types of interaction energies such as dispersion, repulsion, polarization, and dipole/quadrupole interactions. For a given feed the selectivity is a function of the nature of the cation in the zeolite, the surface acidity and the sorbent pretreatment. For instance, large pore size zeolites such as 13X exhibit selectivity for the aromatic components of mixture of aromatics and paraffins. Replacing the polarizing cation by protons reverses the selectivity (14). Similarly in this study the cation of zeolite 13X (sodium) was replaced by other cations, namely H, Zn, Co in order to see the effect on selectivity. The objective is to find two zeolite forms that complement each other. The results are presented in Tables 3-6.

The substitution of the cation changes the selectivity considerably; for instance the capacity of the sodium form for aniline is over 50 mg whereas that of the hydrogen and the zinc forms is 10 and 14 mg respectively. Similarly the capacity of the sodium and hydrogen forms for cyclohexylamine is 50 mg and is only 10 mg for the zinc form. Other compounds such as 1,2,5-trimethylpyrrole are not affected by the exchange. These results suggest the possibility of using two zeolites that complement each other to improve the efficiency of separation. For instance the sodium and hydrogen form seems to be the best combination. Indeed the sodium form is most effective to remove aniline, benzylamine, cyclohexylamine, and to a lesser extent ethylamine but is unable to remove trimethylpyrrole, decylamine, and octylamine. The hydrogen form is most effective to remove decylamine, octylamine, and cyclohexylamine but unable to remove aniline. Such a combination has not been tested in this study.

Conclusion

This study demonstrates the possibility of using zeolites for the large scale selective removal of nitrogenous compounds from petroleum fractions. The results indicate the difficulty of removing all nitrogenous compounds indiscriminately. Larger neutral compounds are not removed to any great extent while smaller basic compounds are removed extensively. This deficiency can be corrected somewhat by modifying the selectivity of the zeolite by cation exchange.

Zeolites were also found to be effective for the selective removal of nitrogenous compounds contained in naphthas. The sorption capacity obtained with naphthas is much lower than expected based on the model compound study. This suggests that non-nitrogenous compounds are competing for the surface sites. More data will be required to identify the competing species and modify the zeolite to inhibit this phenomenon.

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Table 1 - Composition of model solutions

Solution 1		Solution 2	
Compound	ppm N	Compound	ppm N
aniline	30.12	aniline	48.07
1,2,5-trimethylpyrrole	28.20	3-ethylpyridine	48.22
benzylamine	39.79	4-ethylpyridine	49.05
n-octylamine	32.79	n-octylamine	44.40
n-decylamine	27.08	n-decylamine	35.95
quinoline	32.02	1,2,5-trimethylpyrrole	50.76
indole	29.37	cyclohexylamine	54.41
3-methylindole	26.74	benzylamine	51.21
2,2´-dipyridyl	55.58	2,4,6-collidine	48.26
1-phenethylpiperidine	22.88	tri-n-propylamine	34.49
2-phenylpyrydine	24.26	tert-butylamine	51.85
dibenzylamine	26.48		
tetrahydrocarbazole	27.70		
carbazole	25.24		
2-methylacridine	19.40		
3,4-benzacridine	7.85		
2-aminochrysene	13.90		
phenothiazine	29.60		
Total N concentration	518.21		516.67

Table 2 - Naphtha properties

Hydroprocessed	Coker	
Specific gravity 60/60 F	0.74	0.75
Sulphur wt %	0.18	0.18
Carbon wt %	85.98	85.25
Hydrogen wt %	13.45	13.88
Nitrogen wt %	0.005	0.002
Bromide number	24	74
Simulated distillation (wt %)		
Paraffins	55	24.61
Olefins	15	61.79
Naphtenes	19	0.0
Aromatics	10	13.60

Table 3 – Selectivity for zeolite 13X in the sodium form (Na)

Compound	Volume at breakthrough (mL)	Total loading (mg)
1,2,5-trimethylpyrrole	22	12.16
n-decylamine	82	23.23
tri-n-propylamine	82	26.00
n-octylamine	105	30.93
2,4,6-collidine	105	42.76
3-ethylamine	144	47.07
4-ethylamine	160	51.66
cyclohexylamine	162	53.91
tert-butylamine	183	44.77
aniline and benzylamine not broken through		
Total		332.49

Table 4 – Selectivity for zeolite 13X in the hydrogen form (H)

Compound	Volume at breakthrough (mL)	Loading at breakthrough (mg)
aniline	36	9.98
1,2,5-trimethylpyrrole	36	11.74
3-ethylpyridine	45	14.31
4-ethylpyridine	48	15.92
2,4,6-collidine	60	21.29
tri-n-propylamine	78	23.64
n-decylamine	97	32.13
n-octylamine	123	43.56
benzylamine	135	45.85
cyclohexylamine	148	49.09
tert-butylamine not broken through		
Total		267.51

Table 5 - Selectivity for zeolite 13X in the zinc form (Zn)

Compound	Volume at Breakthrough (mL)	Loading at Breakthrough (mg)
cyclohexylamine	20	6.80
1,2,5-trimethylpyrrole	42	12.47
aniline	48	13.83
3-ethylpyridine	56	18.23
tri-n-propylamine	68	20.88
2,4,6-collidine	72	26.31
n-decylamine	74	26.29
4-ethylpyridine	78	25.95
n-octylamine, tert-butylamine, and benzylamine not broken through		
Total		150.76

Table 6 - Selectivity for zeolite 13X in the cobalt form (Co)

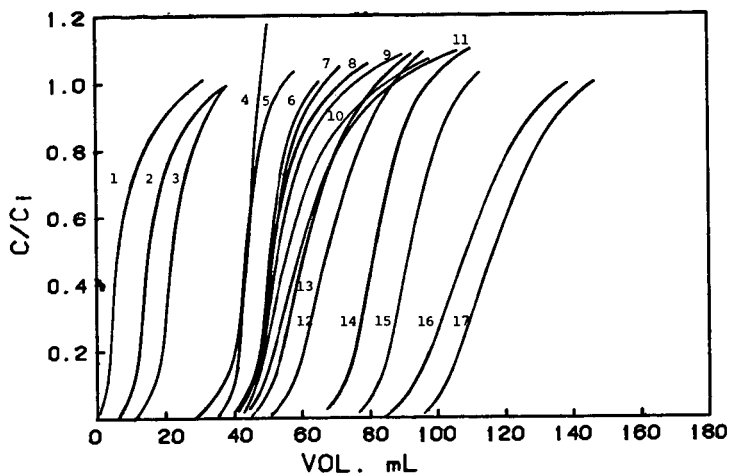| Compound	Volume at Breakthrough (mL)	Loading at Breakthrough (mg)
aniline	16	3.65
1,2,5-trimethylpyrrole	16	4.91
2,4,6-collidine	18	5.28
3-ethylpyridine	18	5.43
4-ethylpyridine	23	7.04
tri-n-propylamine	24	7.37
n-decylamine	67	22.89
n-octylamine	74	25.20
benzylamine	75	25.64
cyclohexylamine	79	27.13
tert-butylamine not broken through		
Total		134.54

FIGURE 1 - Selectivity of sorption of zeolite 13X for a standard mixture.
   1) benzacridine, 2) 1,2,5-trimethylpyrrole, 3) tetrahydrocarbazole,
   4) n-decylamine, 5) 2-methylacridine, 6) aminochrysene, 7) carbazole
   8) n-octylamine, 9) 1-phenethylpiperidine, 10) phenothiazine,
   11) 2-phenylpyridine, 12) 3-methylindole, 13) dibenzylamine,
   14) Indole, 15) quinoline, 16) aniline, 17) 2,2' dipyridyl.
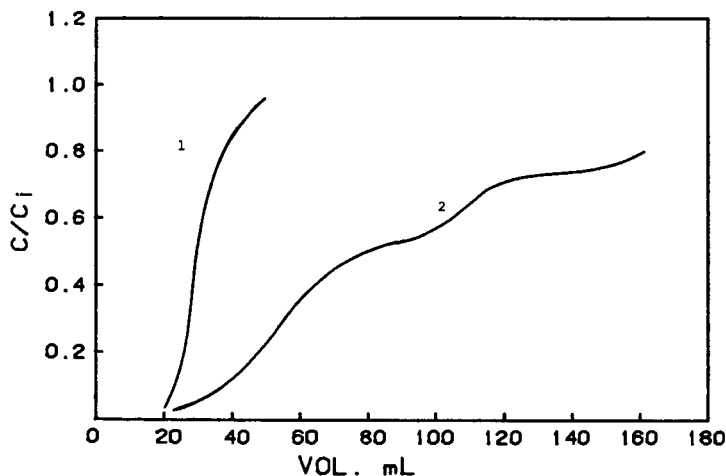   Benzylamine did not elute after 150 mL.

·Fig. 2 - Breakthrough curve for: hydroprocessed naphtha (curve 1)
         and coker naphtha (curve 2) sorbed on zeolite 13X.